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COMMENT

Comment on "Reaction kinetics of humic acid with sodium hypochlorite" by M. C. Sánchez Jimenez, A. Pedraza Dominguez and J. M. Cachaza Silverio, *Wat. Res.* **27**, 815–820 (1993)

Sánchez Jimenez *et al.* (1993) studied the oxidation kinetics of humic acid (HA) with sodium hypochlorite (NaOCl) and presented some useful information on the reaction kinetics. However, there are several errors that may confuse the readers and blemish the quality of this paper.

The fist error concerns the inconsistent initial concentration of sodium hypochlorite ($[NaOCl]_0$). It is labeled as "10 mg/l" in Fig. 4 on p. 818 but is shown as "30 mg/l" in the text on page 818. The E value, which is defined as the ratio of the measured absorbance (A) to humic acid concentration ([HA]), or slope of a linear plot of the absorbance vs. humic concentration, is used to relate the absorbance data presented in Figs 1–4 of this paper to humic acid concentration ([HA]). To verify the E value, synthetic humic acid solutions with concentrations similar to those reported in this paper were prepared using the humic acid (HO161) manufactured by Tokyo Kasei and a Hitachi U-2000 Spectrophotometer was used to measure the absorbance (Chang *et al.*, 1994). The slope or the E value of the linear plot for absorbance using $u.v._{254}$ and $u.v._{257}$ was found to be 2.12×10^{-2} and 2.18×10^{-2}, respectively. These values are close to the E value of 2.494×10^{-2} as listed in Table 1 on page 818 of this paper. Based on these E values as well as data presented in this paper, the initial concentration of sodium hypochlorite ($[NaOCl]_0$) in the label for Fig. 4 in this paper should be 30 mg/l instead of 10 mg/l.

The second error is that Figs 5 and 6 share identical data points and plots as well as x- and y-axis labeling. In this paper, Jimenez *et al.* proposed that the oxidation reaction of humic acid with sodium hypochlorite occurs in two stages. During the first stage, humic acid combines with NaOCl to form chlorinated intermediate products. These products are then completely oxidized in the second stage. The reaction rate constants of these two stages are k_1 and k_2, respectively. An empirical formula has been proposed to relate the measured initial reaction rate (V_0) to k_1, k_2, the initial concentrations of humic acids ($[HA]_0$) and the initial concentration of sodium hypochlorite ($[NaOCl]_0$):

$$V_0 = \frac{k_1[HA]_0[NaOCl]_0}{1 + k_2[HA]_0[NaOCl]_0} \quad (1)$$

Table 1. The ratio of $[NaOCl]_0/V_0$ is re-calculated using data obtained from Table 1 presented by Sánchez Jimenez *et al.* (1993) and the results are shown by numbers without asterisks for the various pH, $[HA]_0$ and $[NaOCl]_0$ values represented in this table by numbers with asterisks

pH	[HA] (mg/l)	[NaOCl] in mg/l 10*	20*	30*
6*	1.0*	1652	1578	2272
	1.5*	1503	1538	2255
	2.0*	1398	1481	2127
	2.5*	1587	1550	2069
7*	1.0*	909	1212	1402
	1.5*	862	1087	1293
	2.0*	893	1092	1293
	2.5*	800	1058	1310
8*	1.0*	1022	943	1149
	1.5*	714	719	1064
	2.0*	699	697	817
	2.5*	581	690	829
9*	1.0*	461	752	796
	1.5*	408	641	771
	2.0*	392	592	785
	2.5*	498	744	1027

Table 2. The ratio of $[HA]_0/V_0$ is re-calculated using data obtained from Table 1 presented by Sánchez Jimenez *et al.* (1993) and the results are shown by numbers without asterisks for the various pH, $[HA]_0$ and $[NaOCl]_0$ values represented in this table by numbers with asterisks

pH	[HA] (mg/l)	[NaOCl] in mg/l 10*	20*	30*
6*	1.0*	165	79	76
	1.5*	226	115	113
	2.0*	280	148	142
	2.5*	397	194	172
7*	1.0*	91	61	47
	1.5*	129	82	65
	2.0*	179	109	88
	2.5*	200	132	109
8*	1.0*	102	47	38
	1.5*	107	54	53
	2.0*	140	70	55
	2.5*	145	86	69
9*	1.0*	46	38	27
	1.5*	61	48	39
	2.0*	78	59	52
	2.5*	124	93	86

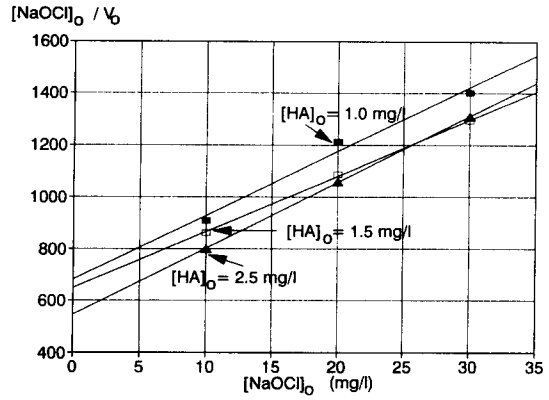

Fig. 1. Plot of $[NaOCl]_0/V_0$ vs $[NaOCl]_0$ for $[HA]_0$ concentrations varying from 1.0 mg/l to 2.5 mg/l (pH = 7). This figure should replace Fig. 5 presented in the paper being discussed (Sánchez Jimenez *et al.*, 1993). Regression analyses of the data plotted yield the following formulas:

$[HA]_0$ = 1.0 mg/l:

$[NaOCl]_0/V_0 = 24.65[NaOCl]_0 + 681.30$ ($R^2 = 0.9828$);

$[HA]_0$ = 1.5 mg/l:

$[NaOCl]_0/V_0 = 21.55[NaOCl]_0 + 649.70$ ($R^2 = 0.9994$);

$[HA]_0$ = 2.5 mg/l:

$[NaOCl]_0/V_0 = 25.50[NaOCl]_0 + 546.00$ ($R^2 = 0.9999$).

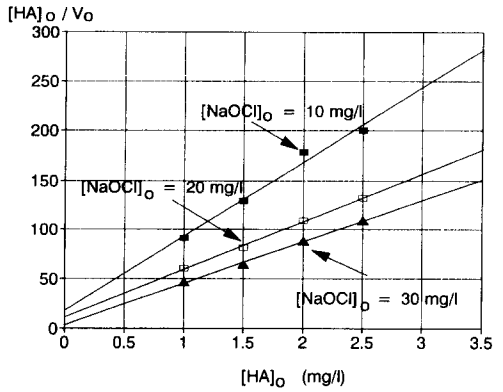

Fig. 2. Plot of $[HA]_0/V_0$ vs $[HA]_0$ for $[NaOCl]_0$ concentrations varying from 10 mg/l to 30 mg/l (pH = 7). This figure should replace Fig. 6 presented in the paper being discussed (Sánchez Jimenez *et al.*, 1993). Regression analyses of the data plotted yield the following formulas:

$[NaOCl]_0$ = 10 mg/l:

$[HA]_0/V_0 = 75.32[HA]_0 + 17.89$ ($R^2 = 0.9796$);

$[NaOCl]_0$ = 20 mg/l:

$[HA]_0/V_0 = 48.56[HA]_0 + 10.94$ ($R^2 = 0.9973$);

$[NaOCl]_0$ = 30 mg/l:

$[HA]_0/V_0 = 42.17[HA]_0 + 3.375$ ($R^2 = 0.9975$).

Depending on whether $[NaOCl]_0$ or $[HA]_0$ is selected, two linearized forms of Eq. 1 can be used for estimating values of k_1 and k_2 as demonstrated by equations (2) and (3).

$$\frac{[NaOCl]_0}{V_0} = \frac{1}{k_1[HA]_0} + \frac{k_2[NaOCl]_0}{k_1} \tag{2}$$

$$\frac{[HA]_0}{V_0} = \frac{1}{k_1[NaOCl]_0} + \frac{k_2[HA]_0}{k_1}. \tag{3}$$

In this paper, a plot of $[NaCOl]_0/V_0$ vs $[NaOCl]_0$ [equation (2)] is shown in Fig. 5 while Fig. 6 shows a plot of $[HA]_0/V_0$ vs $[HA]_0$ [equation (3)]. Since different parameters are used for plotting Figs 5 and 6, these two figures should not be identical as displayed in this paper.

In order to derive the correct plots of Figs 5 and 6, the numbers presented in Table 1 of this paper are used to re-calculate the ratio of $[NaOCl]_0/V_0$ and $[HA]_0/V_0$. The results are listed in Tables 1 and 2 of this discussion. From these results, $[NaOCl]_0/V_0$ (pH = 7) is plotted vs $[NaOCl]_0$ in Fig. 1 and $[HA]_0/V_0$ (pH = 7) vs $[HA]_0$ in Fig. 2. Comparison of Figs 1 and 2 presented in this discussion and Figs 5 and 6 in the paper being discussed indicates the following errors:

(1) The straight line plots in Fig. 5 are erroneously labeled with the initial humic acid concentration. The order should be 1.0, 1.5 and 2.5 mg/l from the top to the bottom plot as displayed in Fig. 1 of this discussion.
(2) All data points and plots in Fig. 6 are erroneously identical to those shown in Fig. 5, and scales for both x- and y-axis are wrong. Additionally, the plots are erroneously labeled with the initial sodium hypochlorite concentration. This figure should be placed by Fig. 2 as presented in this discussion.

Other minor errors include inconsistent labeling for the initial reaction rate (V_0) and the initial concentration of humic acids ($[HA]_0$) in equations (5), (6) and (7). The term "[HA]" in equation 5 should read "$[HA]_0$" and "$[V_0]$" in equations (6) and (7) should be "V_0".

REFERENCES

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